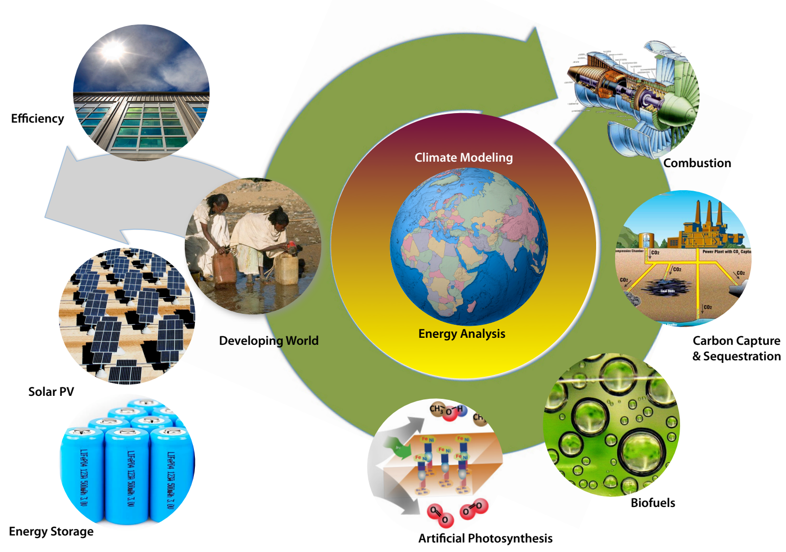
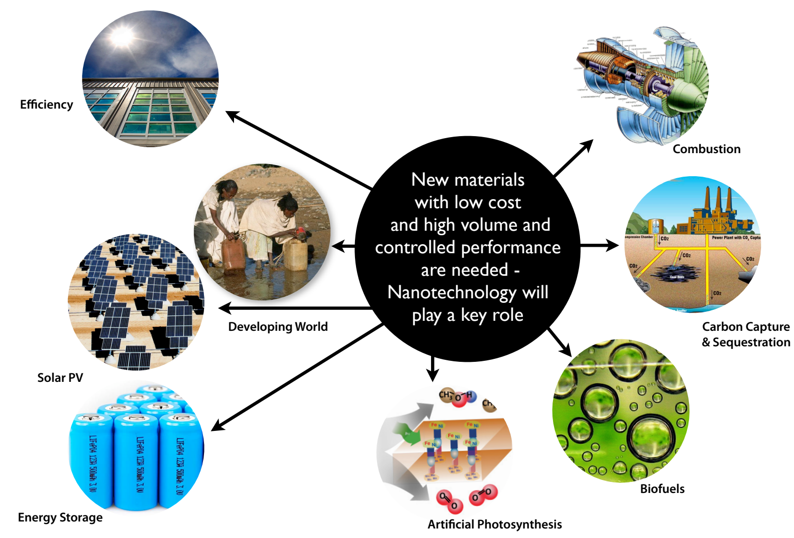
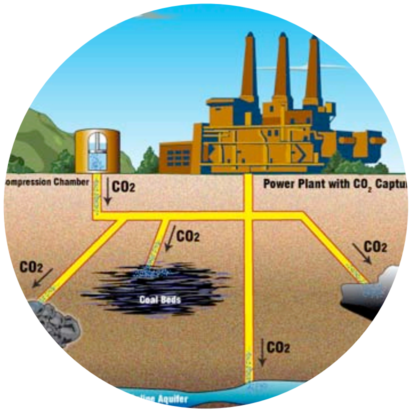
Carbon Cycle 2.0 Initiative at Berkeley Lab



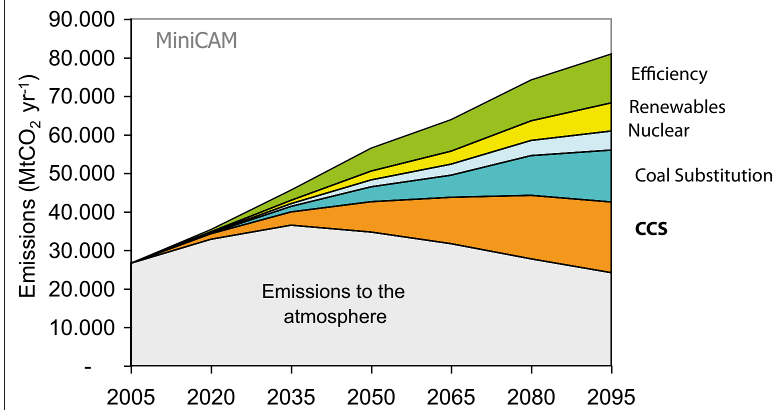
Nanoscience and nanotechnolgy connections...





Carbon Capture & Sequestration

Carbon Capture - a necessary part of the solution

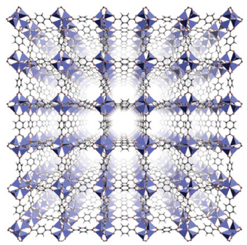


Cost of Carbon Capture today:
\$70-80 /ton of CO2; 7-8 c/kWh
Parasitic energy of 25-30%

Source: IPCC

~0.0009 Tons CO2/kWh in Coal Generation

Carbon Capture - Novel Nanomaterials

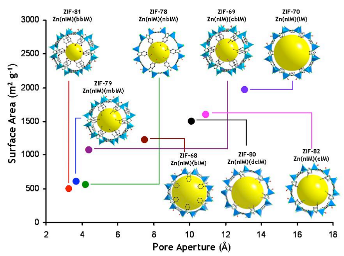


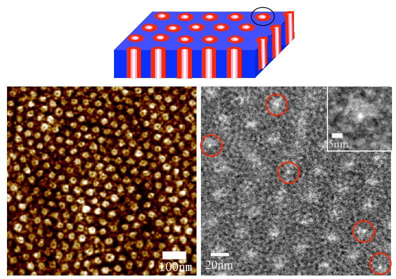
Metal Organic Frameworks

Zeolitic Imidizolate Frameworks

Engineered Polymer Membranes

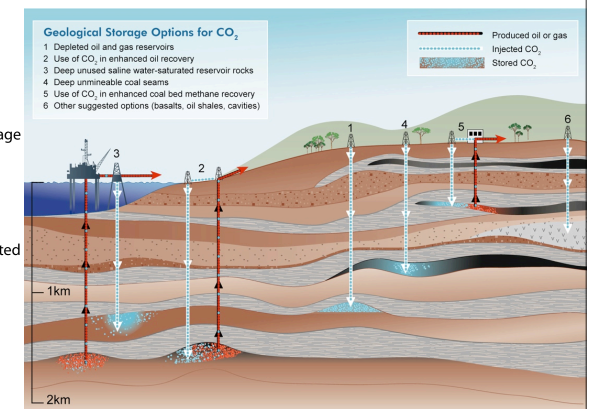
Advanced Computation



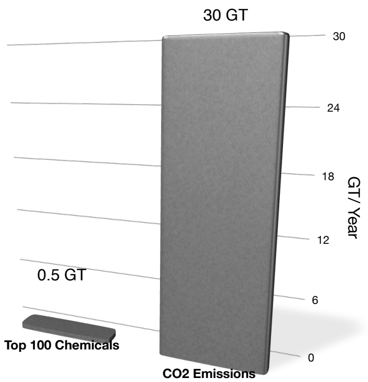


Carbon Sequestration

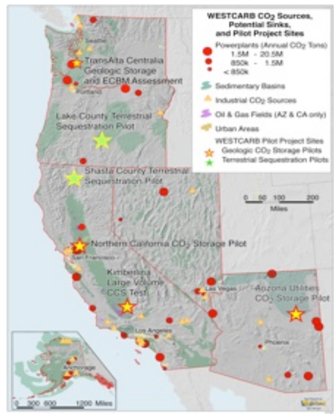
- Successful CCS involves both capture and storage
- Capture is the expensive part
- Sequestration is the "risky" part
- Mismatch in generation and storage locations
- Limitations in global storage capacity
- Geologic sequestration = integrated hydrological, geochemical and geophysical R&D



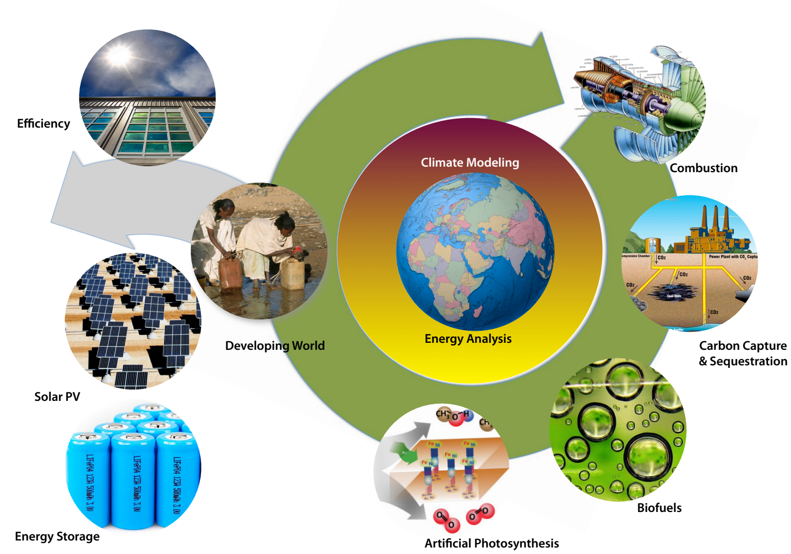
Carbon Capture and Sequestration
- scale of the problem



WESTCARB Pilot Sites

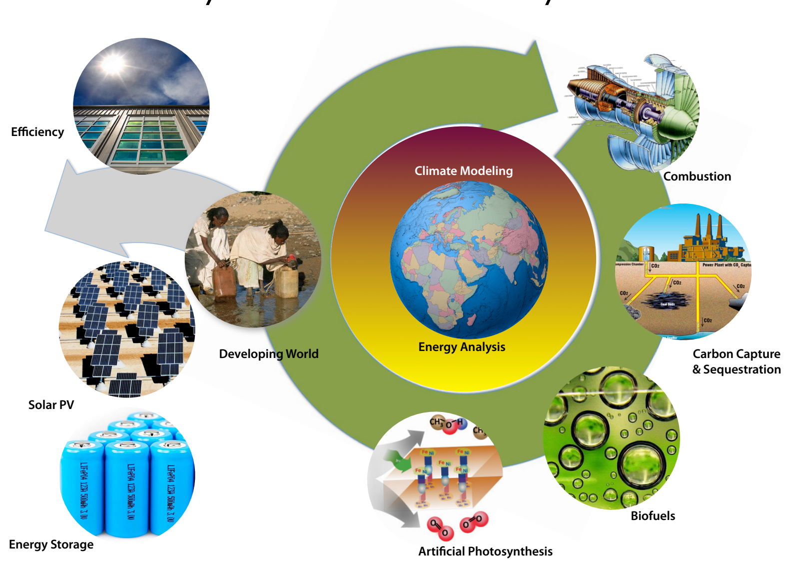


Carbon Cycle 2.0 Initiative at Berkeley Lab

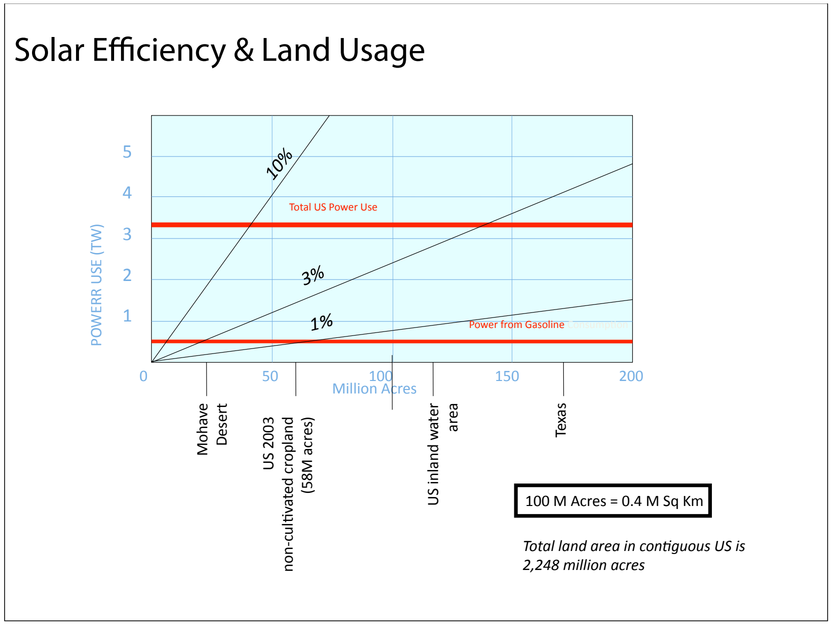


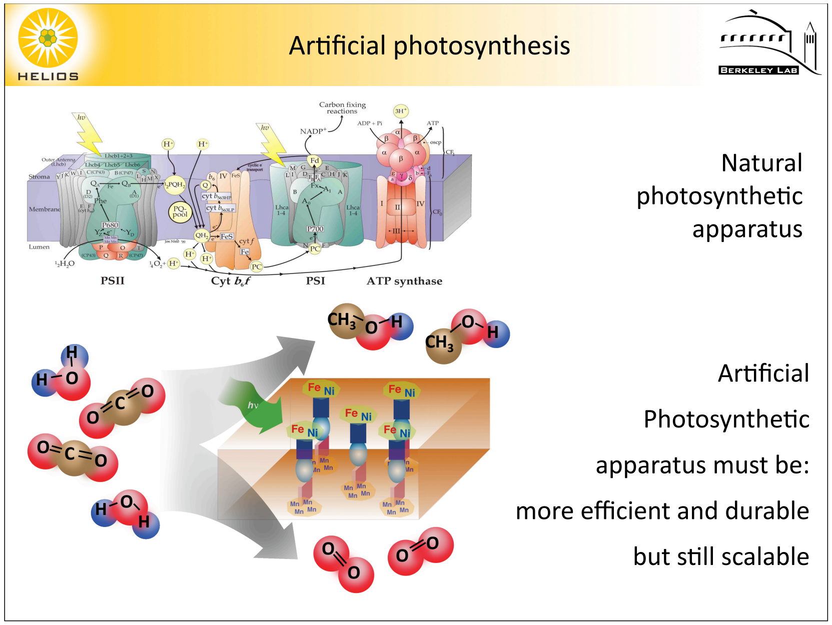
look for simpler westcarb – larrry myers

Carbon Cycle 2.0 Initiative at Berkeley Lab



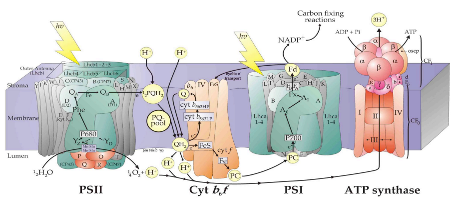
Biofuels

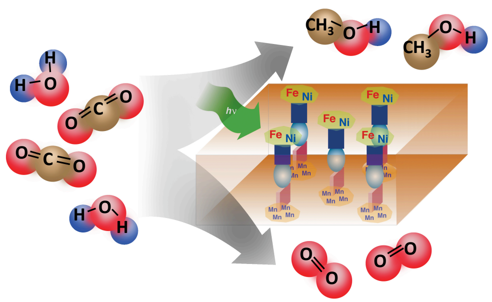




Speak toward goal of creating fuels from sunlight with >1% efficiency with 10 year target for demonstration

Why Nano?



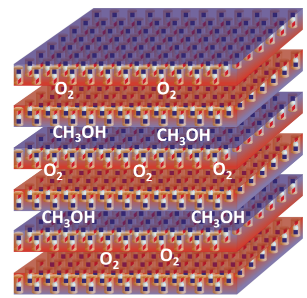


•High density of reactants (photo-generated charges) leads to more products

•10 k_BT dissipation required to ensure directionality of energy flow

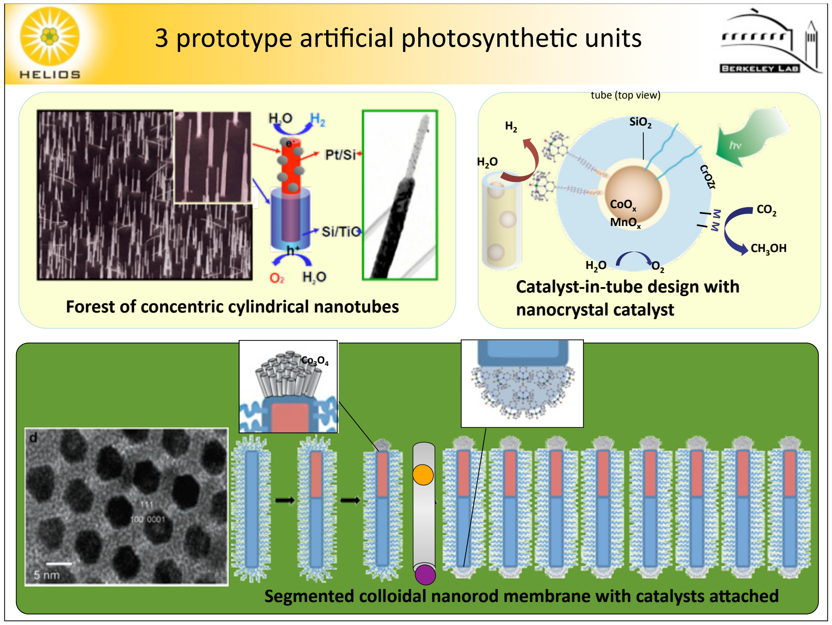
•Match solar flux

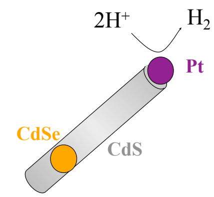
Match catalytic activity with solar flux



Planes of membranes holding vertically aligned PV elements with catalysts attached top and bottom

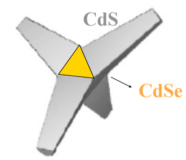
- The solar flux is 2 to 5 kwH/m^2/day
- This corresponds to ~1500 solar photons/nm^2/sec at peak
- To match this flux, we need to arrange catalysts with an areal density and turnover rate of 100-200/nm^2/sec





Hydrogen production from seeded quantum rods

Lilac Amirav, Matt Sheldon, Jen Dionne

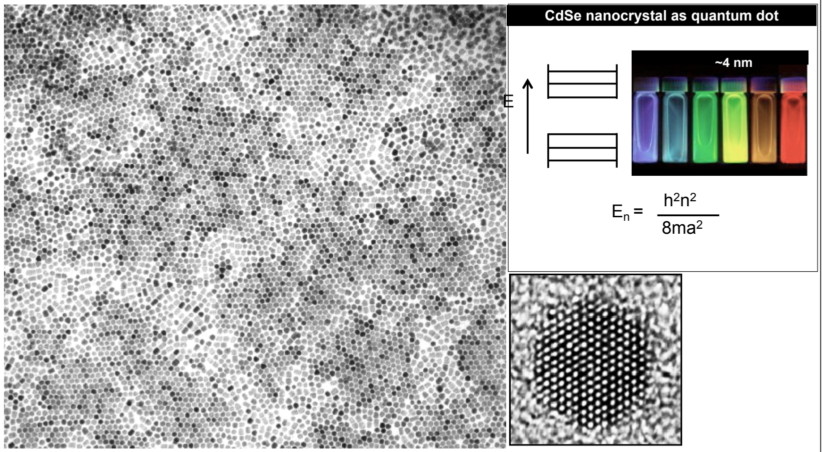


Tetrapod luminescent strain gauge

Charina Choi, Kristie Kotki

Paul Alivisatos, Materials Science Division, Lawrence Berkeley Lab
Department of Chemistry and Materials Science and Engineering, UC Berkeley

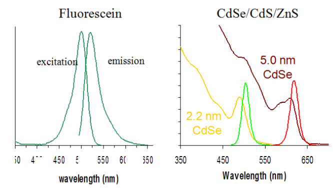
Artificial atom concept and its impact in the chemistry of materials

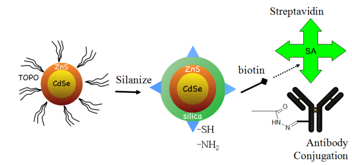


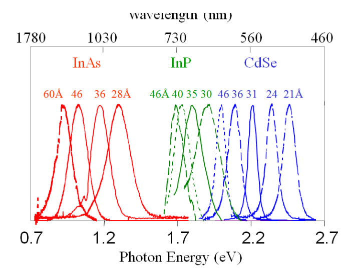
… many scaling laws for size-dependent properties:

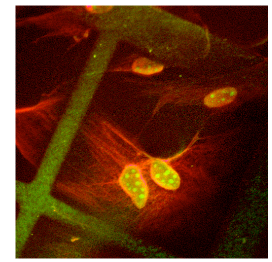
band gap, melting temperature, charging energy…

Quantum Dot Labeling for Biological Imaging





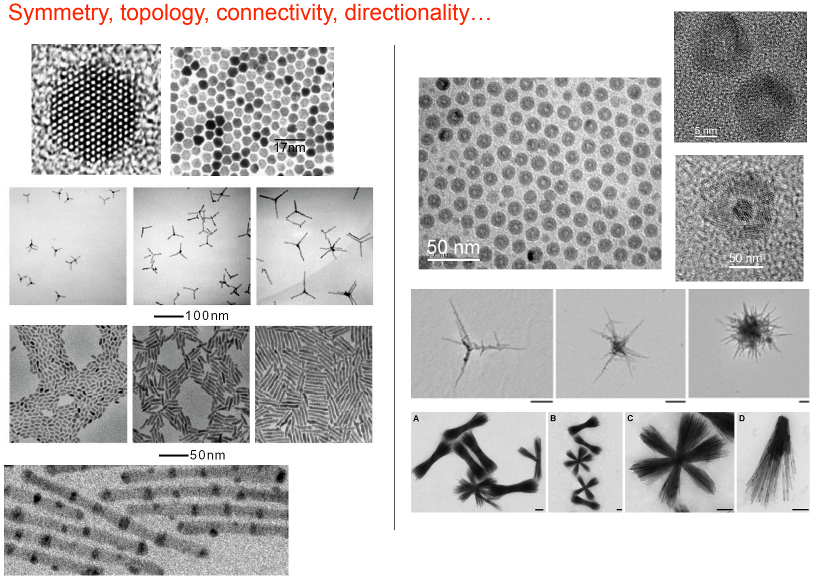




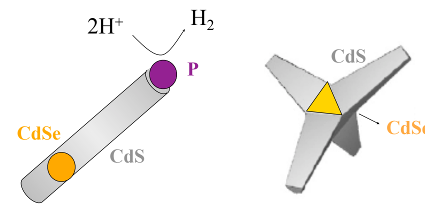
Bruchez, M.; Moronne, M.; Gin, P.; Weiss, S.; Alivisatos, A. P., *Science* **1998**, *281*, 2013-2016.

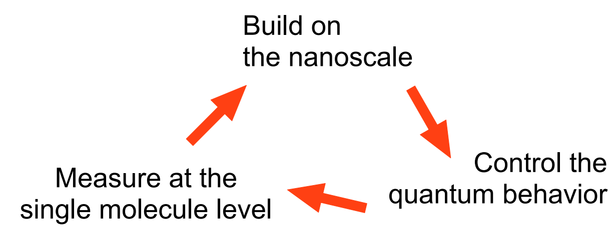
Chan, W. C. W.; Nie, S. M., Science **1998**, *281*, 2016-2018.

Artificial Molecules - quantum controlled nanostructures with designed Symmetry, topology, connectivity, directionality…

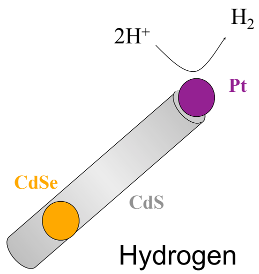


The nanoscience approach to functional materials





Seeded rod prototype for solar fuel

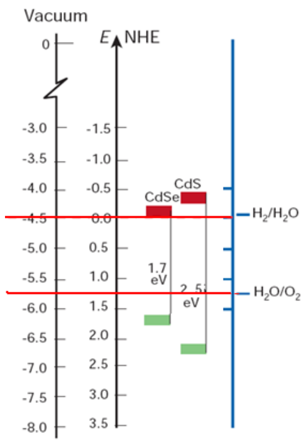


Hydrogen production

- •Seeded rods - built in asymmetry
- •Hydrogen production experiments
- •Single photocatalyst experiments
- •Electrical studies of metal-semiconductor contact in individual nanorods

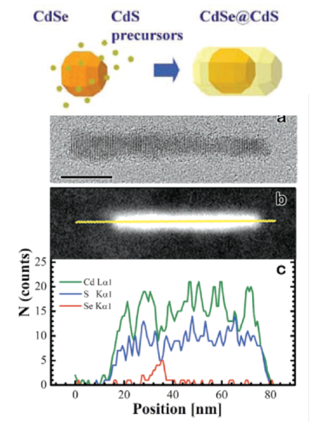
Build on the nanoscale
Control the quantum behavior
Measure at the single molecule level

CdSe/CdS Nanoheterostructures



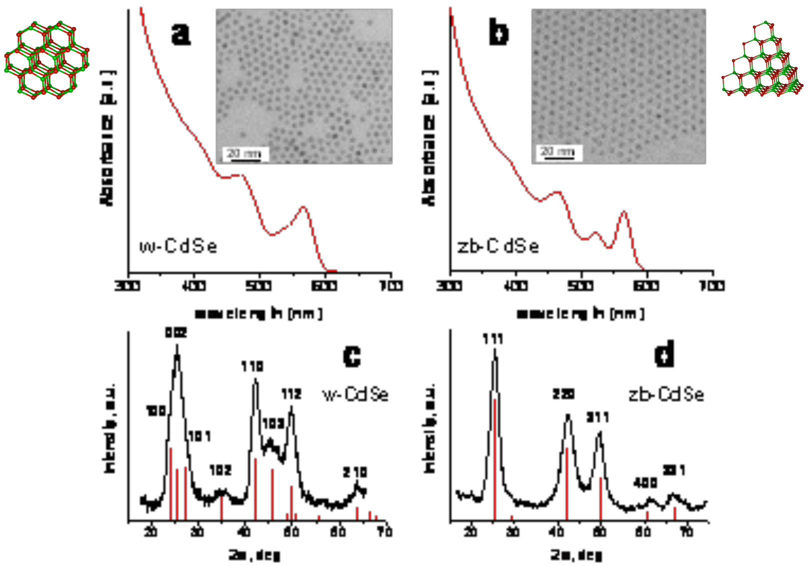
Talapin [2003+2007], Carbone [2007]

Weller Manna Banin Feldman

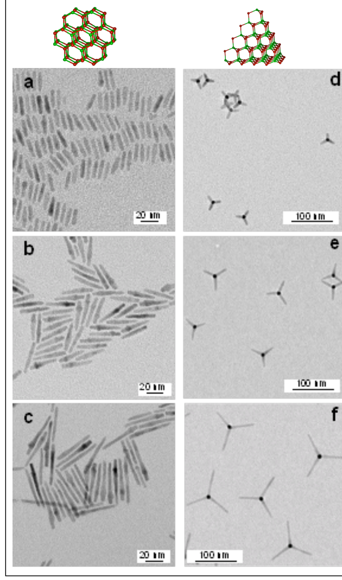


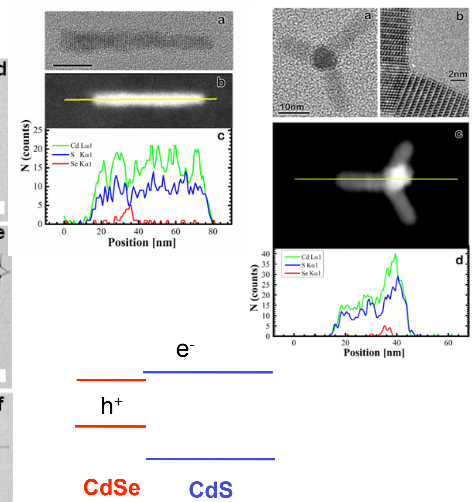
Peng, Schamp, Kadavanich, Alivisatos, Epitaxial growth of highly luminescent CdSe/CdS core/shell nanocrystals with photostability and electronic accessibility. J. Am. Chem. Soc. (1997) vol. 119 pp. 7019-7029

Seeded Growth from Wurtzite and Zincblende CdSe Seeds



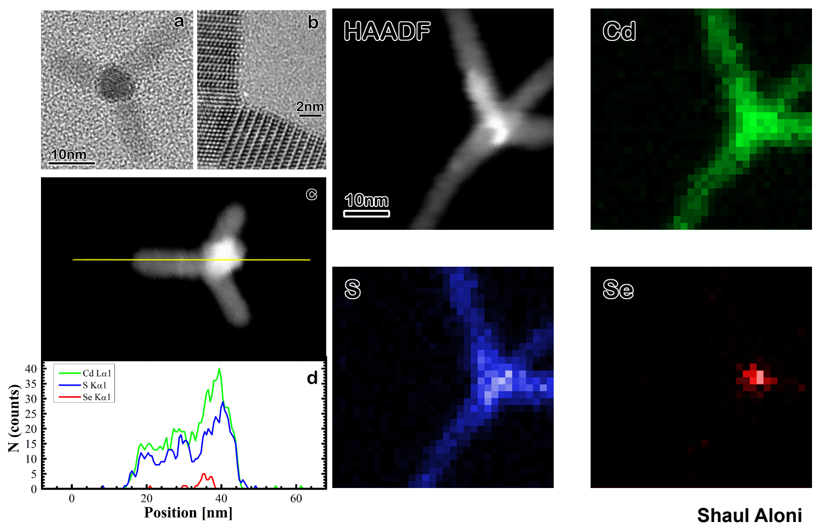
Seeded dot growth of rods and tetrapods



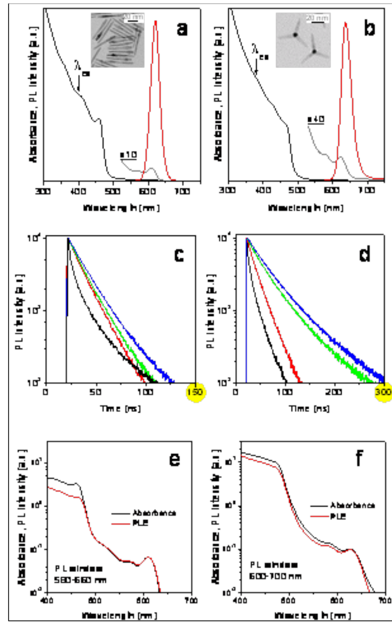


Dmitri V. Talapin, James H. Nelson, Elena V. Shevchenko, Shaul Aloni, Bryce Sadtler, and A. Paul Alivisatos Nano Lett (2007) p 2951

Structural and compositional analysis of the seeded tetrapods



Shaul Aloni



Optical properties of seeded rods/tetrapods

Electron delocalizes into CdS regions

High quantum yields
(>80% for rods, >60% for tetrapods)

Near exponential decays

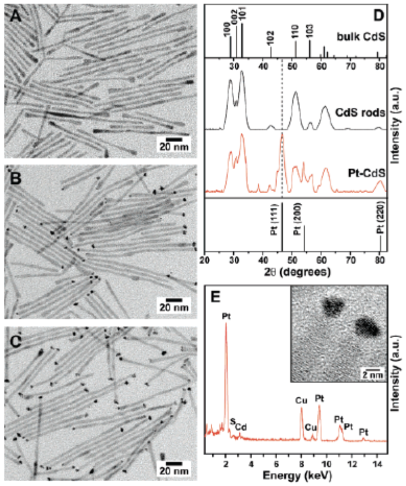
Longer arms -→ slower radiative rate

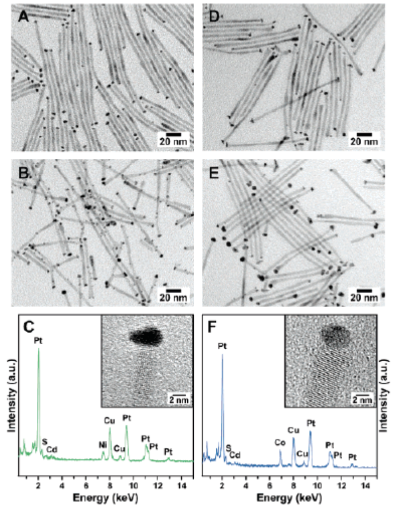
Absent symmetry breaking electrodes,
Photoexcited charges “fall”
into the central dot

Absorbance as large as10^8 M-1cm-1

Dmitri Talapin and Jimmy Nelson

Direct growth of Au/Pt/Co/Ni on CdS Nanorods

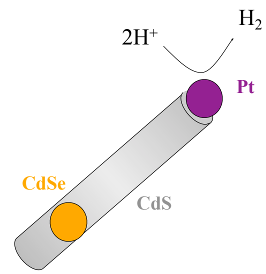


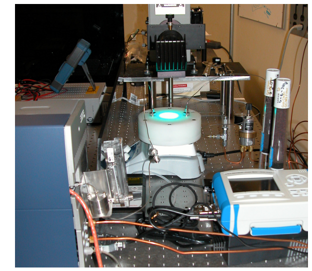


Uri Banin, Jerusalem, Taleb Mokari, Molecular Foundry

Susan Habas, Peidong Yang, Taleb Mokari, J. Am. Chem. Soc. (2008) vol. 130 pp. 3294-3295

Hydrogen production from seeded rods w/ Pt



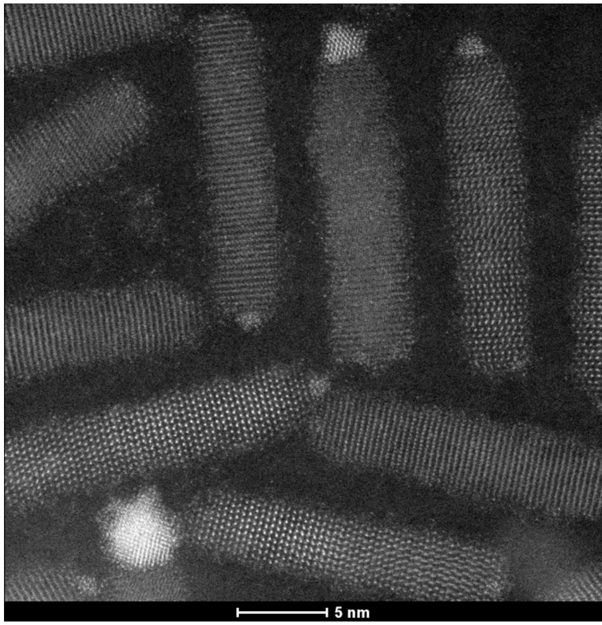


Extensive prior work on CdS/Pt systems:

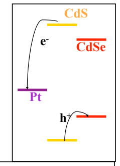
Ningzhong Bao, Liming Shen, Tsuyoshi Takata, and Kazunari Domen *Chem. Mater.*, **2008**, 20 (1), 110-117

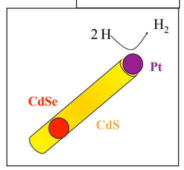
Jean Francois Reber, and Milos Rusek *J. Phys. Chem.*, **1986**, 90 (5), 824-834

Lilac Amirav

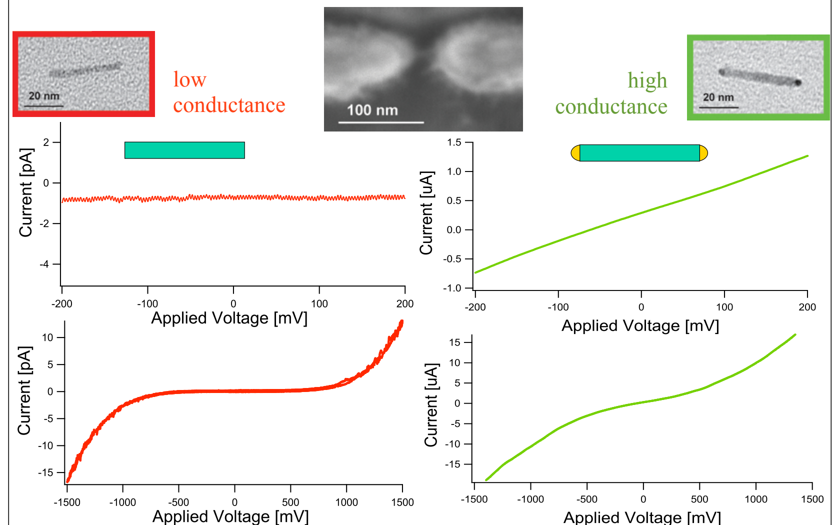


Pt growth
on the tips
of the
seeded
nanorods





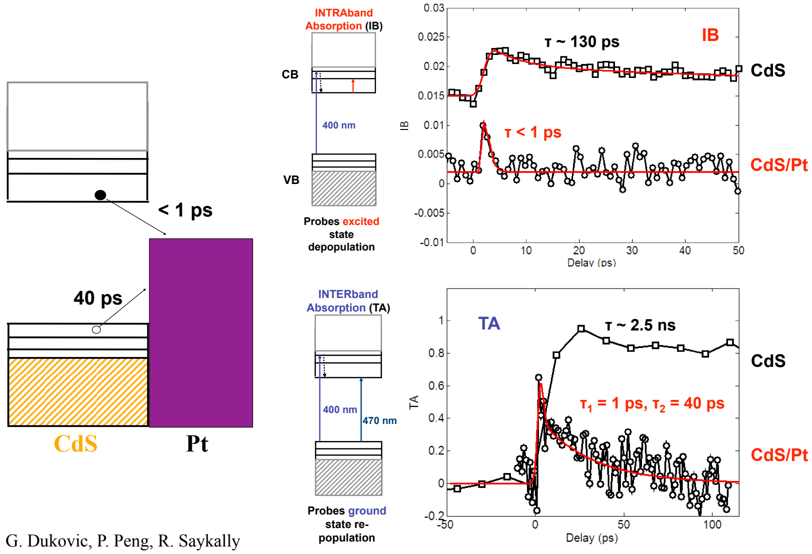
Transport through trapped nanorods-
much higher currents flow through nanorods with soultion grown contacts



Matt Sheldon, Taleb Mokari

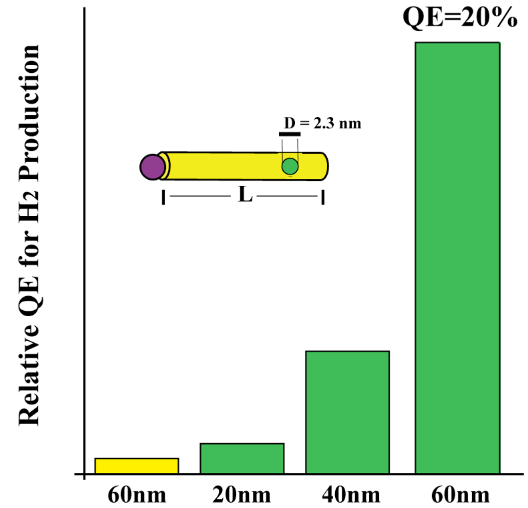
Recombination of Charge Carriers (no seed)

Is the charge separation long-lived (on the time scale of the chemistry)?



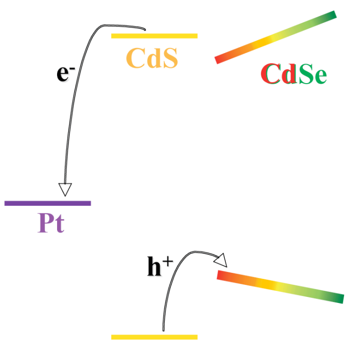
G. Dukovic, P. Peng, R. Saykally

Hydrogen Production Yield Increased in Longer Seeded Rods



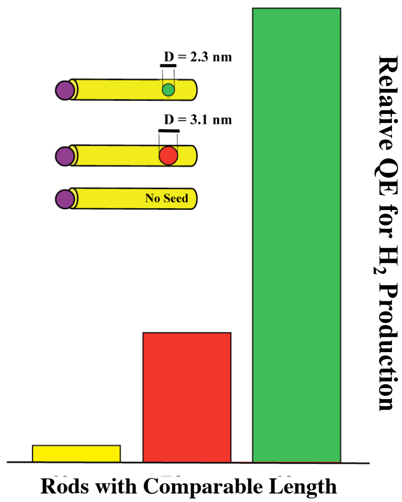
mirav and Alivisatos. JPC Letters 2010

Improved Photocatalytic Efficiency With Smaller Seeds

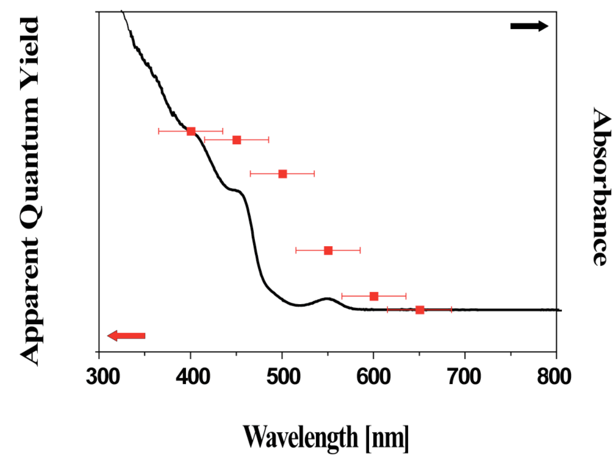


Banin 2009

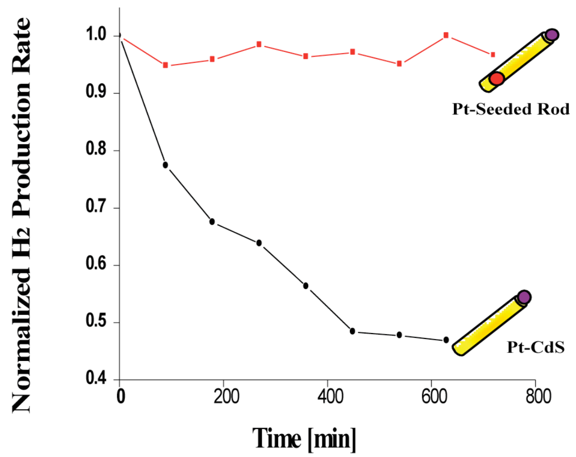
Improved charge separation



Excitation spectrum for the hydrogen production

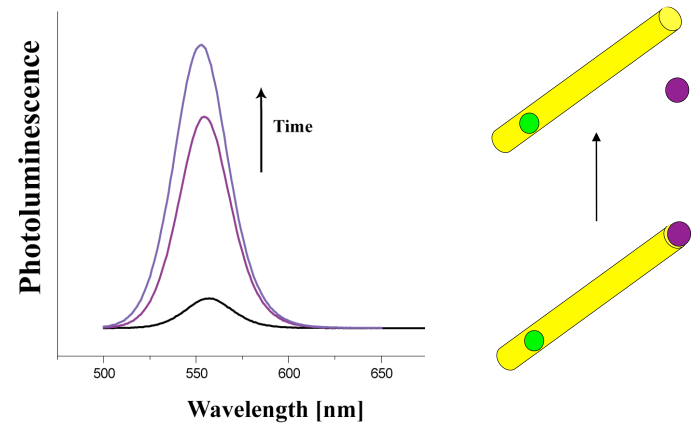


Improved Stability of seeded versus non-seeded rods

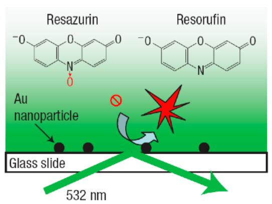


Luminescence and Stability

The interface between the CdS and the Pt is the first to degrade

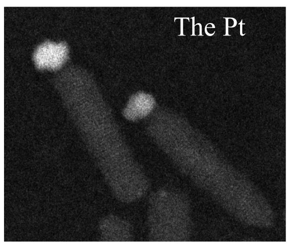


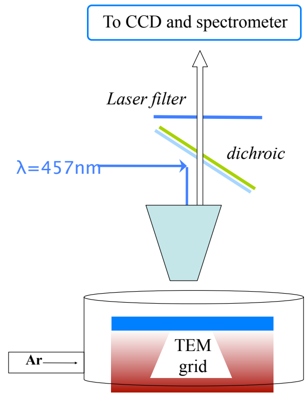
Photocatalysis, One Nanocrystal at a Time…



Au-catalyzed reduction of S to P: One reaction pathway is observed in ensemble, but 3 are present in single-particle studies

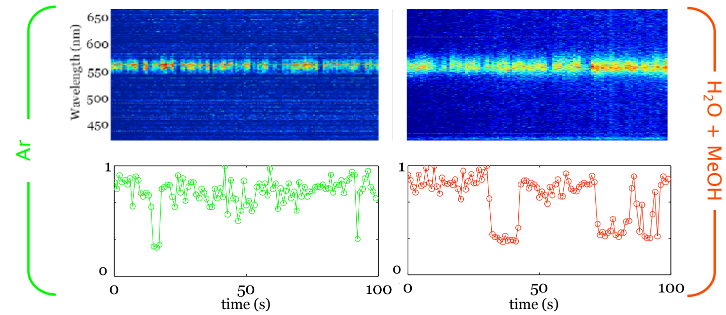
Xu, Chen, Nature Materials 7 (2008)

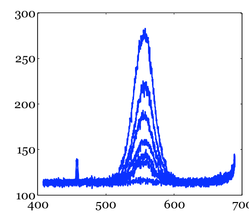


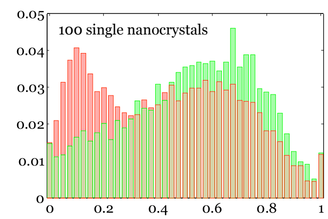


Jen Dionne and Lilac Amirav

Single particle blinking during catalysis





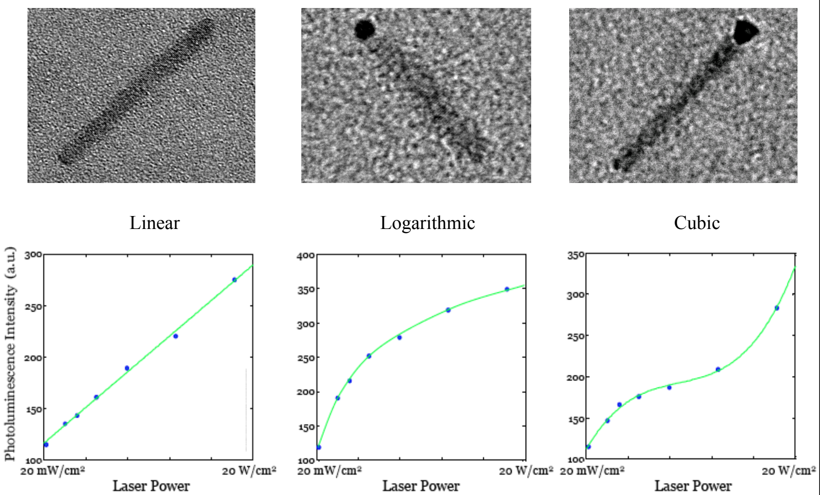


Ar – more time on: radiative recombination favored

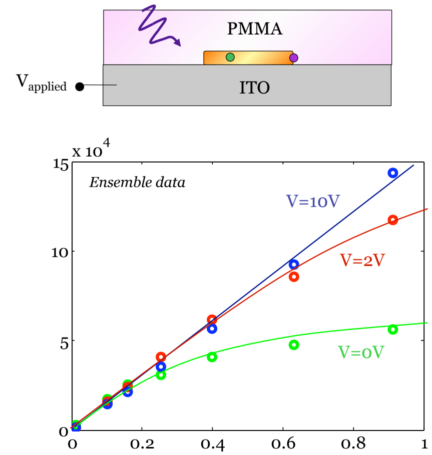
H_2O/MeOH – more time off: electron is transferred to Pt for catalysis

Jen Dionne, Lilac Amirav

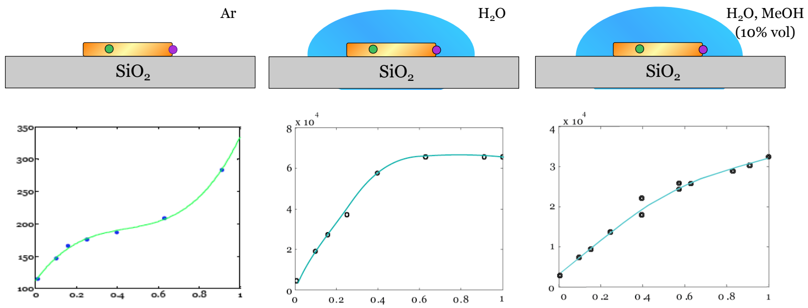
Fluence-Dependent Single Particle Emission Data



Gate Voltage can restore the linear behavior



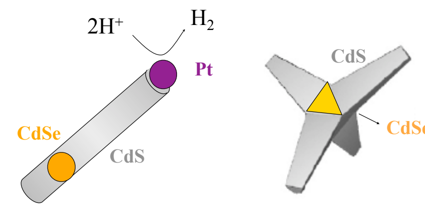
Fluence-Dependent Data During Catalysis



- In the presence of water, the Pt can not reach electron saturation
- The electrons are used by the water faster than they are transferred onto the Pt.
- These experiments can give us first insights into the rate of the catalytic reactions

In the presence of water, the cubic trend disapears for 97% of the particles…

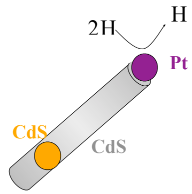
The nanoscience approach to functional materials



Build on the nanoscale

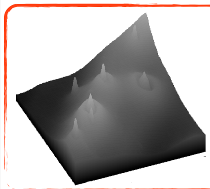
Control the quantum behavior

Measure at the single molecule level



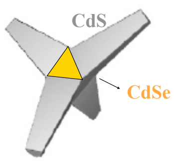
Hydrogen production from seeded quantum rods

Lilac Amirav, Matt Sheldon, Jen Dionne



Cation Exchange in Seeded Nanorods

Prashant Jain, Haimei Zheng

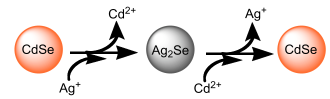


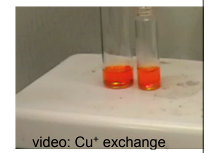
Tetrapod luminescent strain gauge

Charina Choi, Kristie Kotki

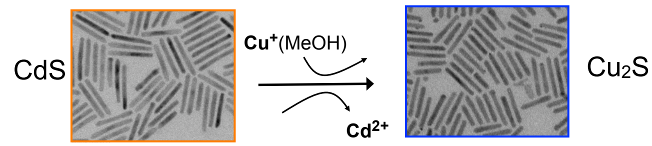
Cation exchange in nanocrystals

Fully reversible

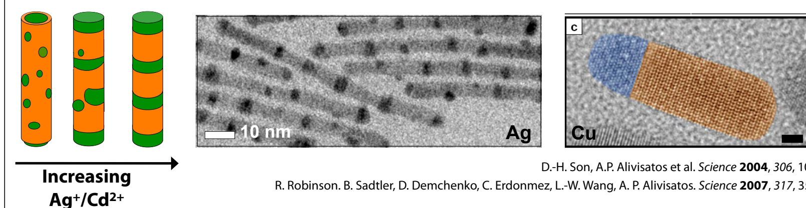




Shape preserving



Partial exchange produces controlled hetero-structures

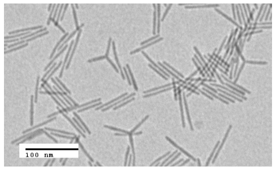


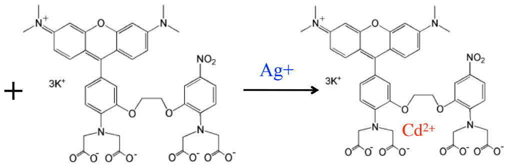
D.-H. Son, A.P. Alivisatos et al. *Science* **2004**, *306*, 1009.

R. Robinson. B. Sadtler, D. Demchenko, C. Erdonmez, L.-W. Wang, A. P. Alivisatos. *Science* **2007**, *317*, 355

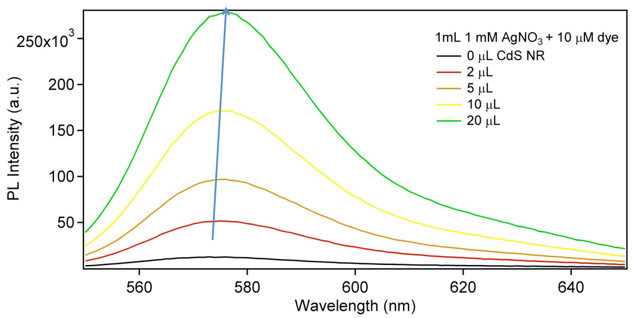
Fluorescence Detection of Ion Exchange

Cadmium sulfide nanorods

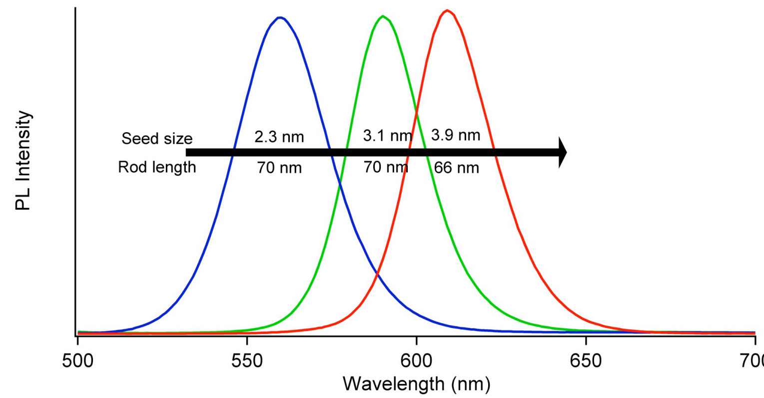




J. Li, J. Ge, T. Zhang, Y. Yin, W. Zhong, Angew. Chem. 2009, 121, p1616

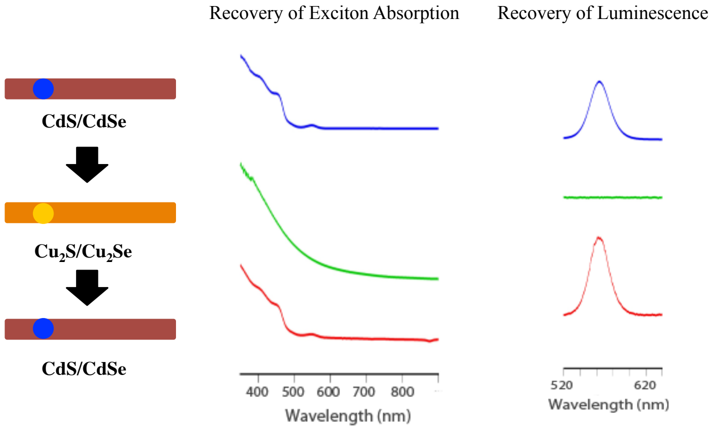


Recall that for seeded rods, seed size critically affects emission band position



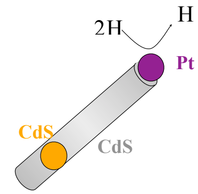
Prashant Jain, Lilac Amirav

Anionic lattice and interface fully conserved through double cation exchange



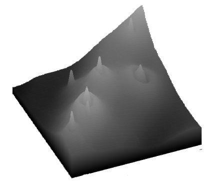
Route for otherwise inaccessible heterostructures

Prashant Jain, Lilac Amirav



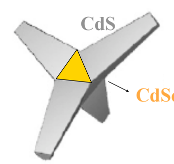
Hydrogen production from seeded quantum rods

Lilac Amirav, Matt Sheldon, Jen Dionne



Imaging Cation Exchange in Single and Seeded Nanorods

Prashant Jain, Haimei Zheng

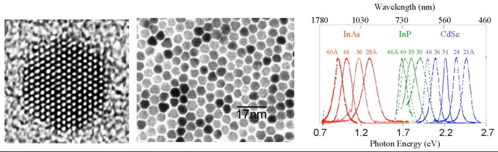


Tetrapod luminescent strain gauge

Charina Choi, Kristie Kotki

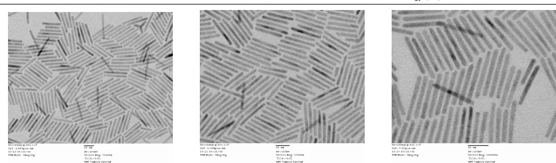
From “dots” to rods and then trees

Dots



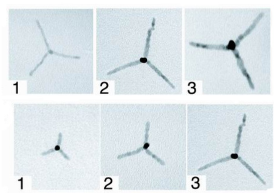
Science 27
933 (1996)

Rods

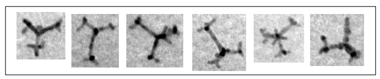


Nature **2000**
404, 59-61.

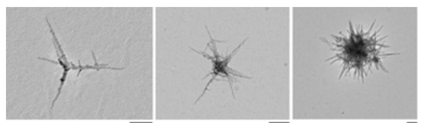
Branched



Nature Materials **2** 382 (2003).

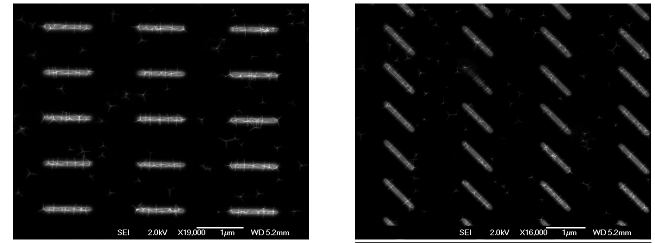


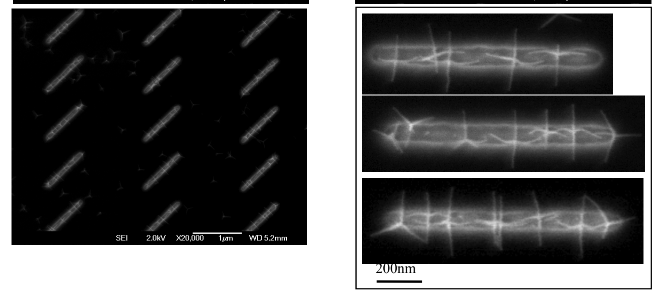
Nature **430**
190 (2004)



Nano Letters 5 2164 (2005).

Tetrapod Deformation: press onto trench walls with capillary forces

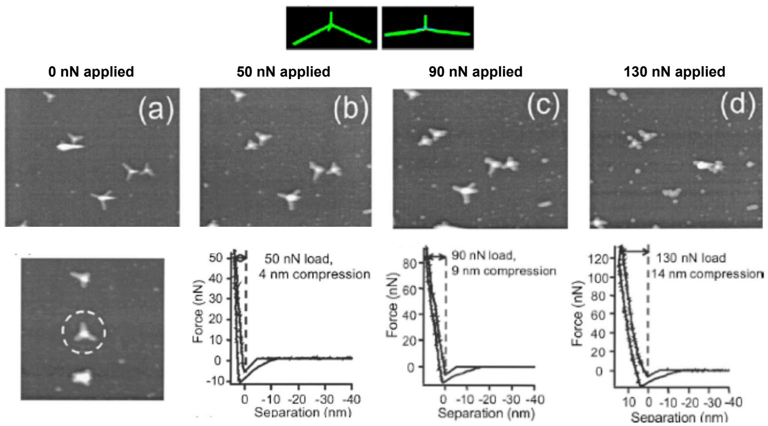




Y. Cui, Y., M. T. Björk, J. A. Liddle, C. Sönnichsen, B. Boussert and A. P. Alivisatos
"Integration of colloidal nanocrystals into lithographically patterned devices." Nano Letters **4**(6): 1093-1098 (2004).

1-100 nN force bends tetrapod arms

Arm bending has been observed experimentally on CdTe tetrapods with ~130 nm arms

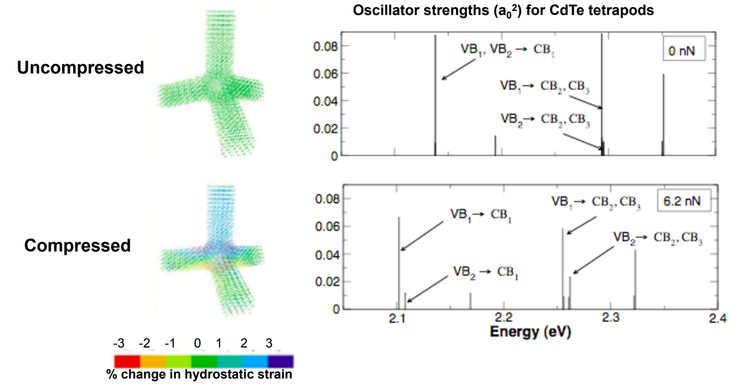


force loaded on the circled tetrapod | arm bending k = 12.5 N/m | arm bending k = 10 N/m | tetrapods irreversibly damaged

Fang, Prof. Miquel Salmeron *J. Chem. Phys*. 2007

Arm bending induces electronic structure changes

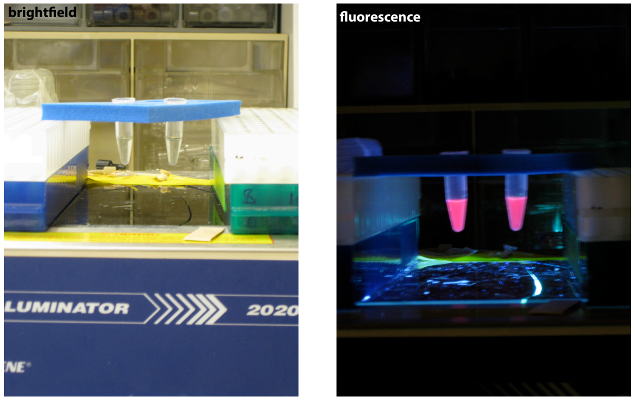
A 35 meV red-shift is theoretically calculated for tetrapods with ~5 nm arms



Tetrapods as an optical strain gauge for forces ~1-100 nN?

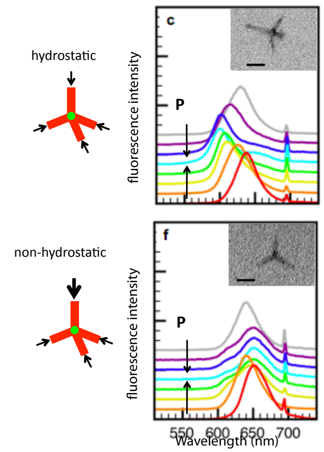
Schrier, and Lin Wang Wang *J. Nanotech. Nanosci*. 2008

Highly luminescent seeded tetrapods, stable in biological media

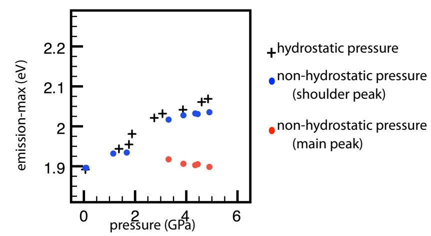


the bending of tetrapod arms does shift PL red (slightly)

experiment: use a **diamond anvil cell** to pressurize tetrapods
in a **hydrostatic** (1:1 pentane:isopentane) or **non-hydrostatic** (toluene) medium.



An optical red-shift is observed for tetrapods which are asymmetrically compressed



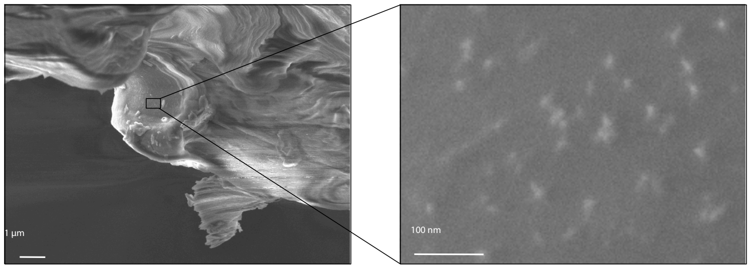
However, we still need a calibration.

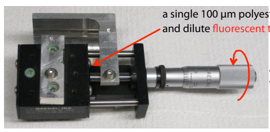
Choi et al. *Nano Lett.* 2009

Both tubes have Shimon Weiss peptide ligands ending in (PEG)6-OH and (PEG)6-COOH. The tube on the left has a Shimon Weiss ligand ending in KGRGDSP and the tube on the right has a ligand ending in KGRDGSP.
The ratio is ~1300:100:100 OH:COOH:RGD or RDG ligands per particle surface.

Talk ab this slide more– make note of the things here, ruby peak, blue-shift, shoulders, TEM insets from after the experiment, etc.
At the end, conclude– we still need a calibration!

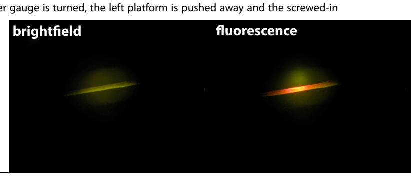
SEM of Tetrapods in polyester



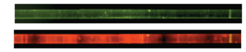


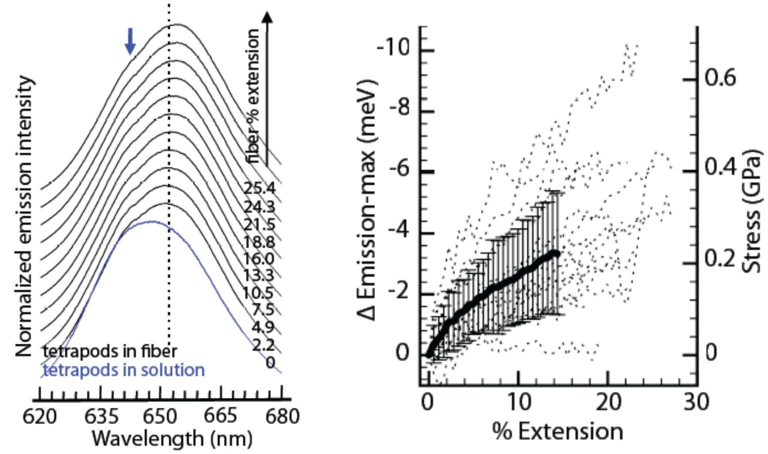
a single 100 µm polyester fiber is held in place by two screws, and dilute fluorescent tetrapods in toluene are injected in

as the micrometer gauge is turned, the left platform is pushed away and the screwed-in fiber is stretched

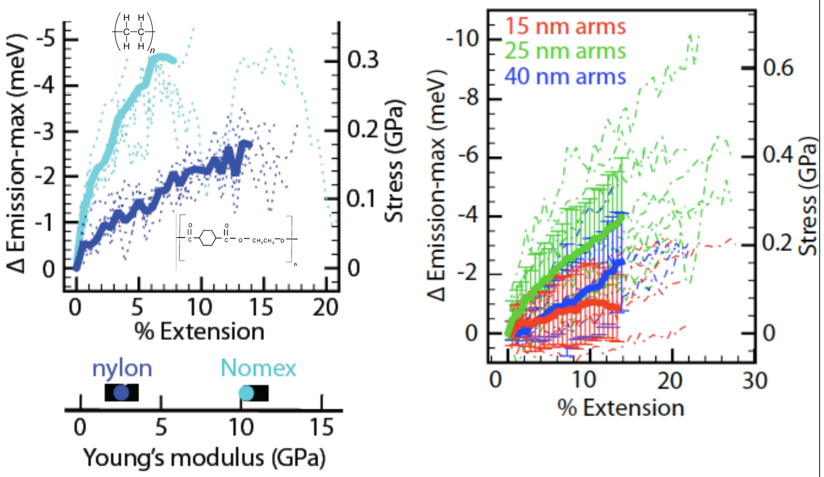


Shift of tetrapod PL in a polyester fiber as it is stretched

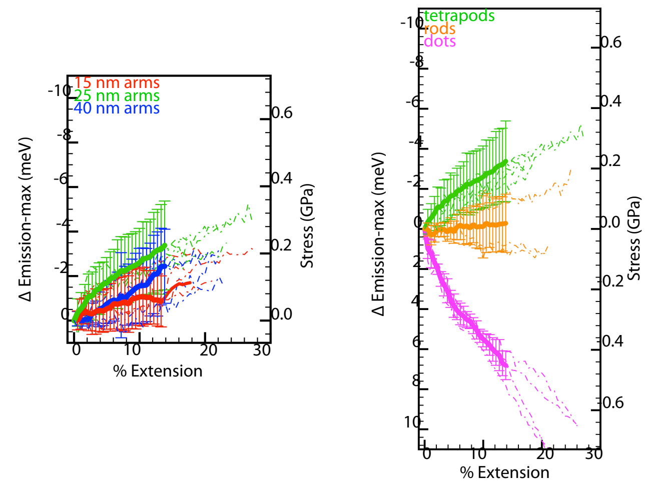




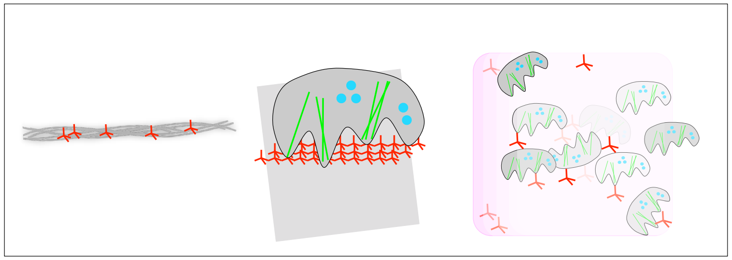
Calibration of the tetrapod strain sensor



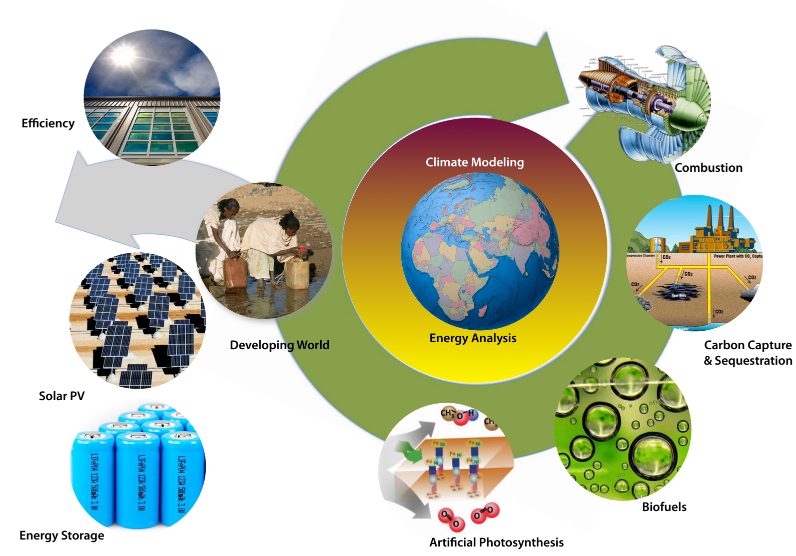
Tetrapods are well-suited for strain-sensing

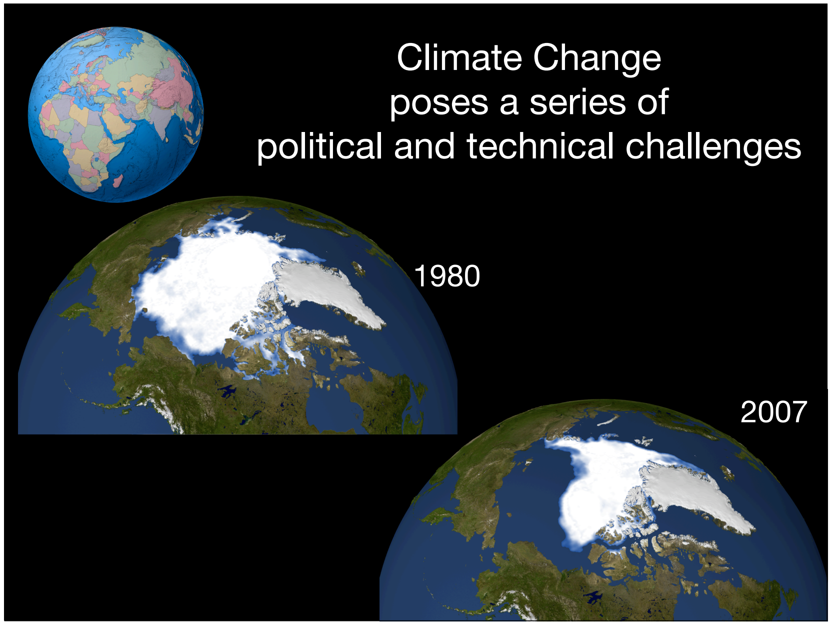


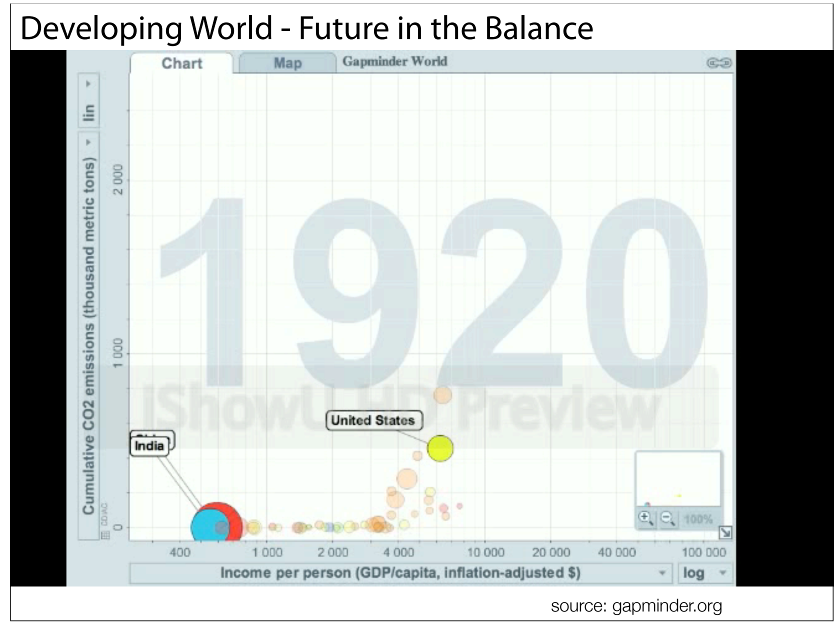
Biological applications of the tetrapod strain sensor

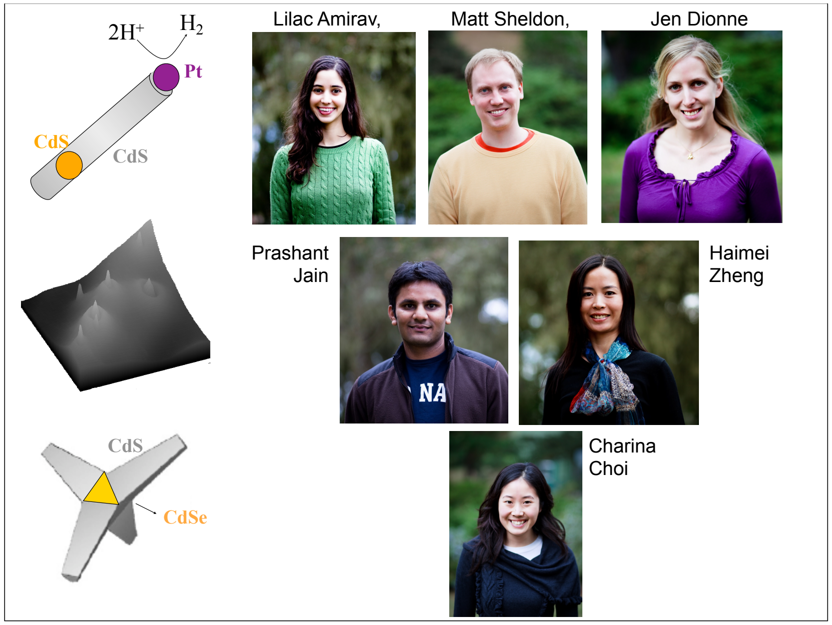


Carbon Cycle 2.0 Initiative at Berkeley Lab




Climate Change
poses a series of
political and technical challenges
1980
2007


Developing World - Future in the Balance
Chart
Map
Gapminder World
lin
Cumulative CO2 emissions (thousand metric tons)
1920
United States
India
400
1 000
2 000
4 000
10 000
20 000
40 000
100 000
Income per person (GDP/capita, inflation-adjusted $)
log
source: gapminder.org



2H+
H2
Pt
CdS
CdS
CdS
CdSe
Lilac Amirav,
Matt Sheldon,
Jen Dionne
Prashant Jain
Haimei Zheng
Charina Choi